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A unified mechanism of the combustion reactions of lignocellulosic fuels

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ABSTRACT

Thermogravimetric curves in air, measured for beech and fir wood and three agro-industrial residues (hazelnut shells, olive husks and wheat straw) at different heating rates (5–40 K/min), are subjected to kinetic evaluation. It is shown that a five step mechanism (three reaction for the devolatilization stage and two reactions for the combustion stage) provides good predictions in all cases. Moreover, for the combustion stage (amounts of volatile released between 25 and 40%) the activation energies are the same (113 and 183 kJ/mol). On one side, the devolatilization stage is also very similar for the residues which require activation energies of 125, 170 and 164 kJ/mol for the pseudo-components hemicellulose, cellulose and lignin. On the other, the behavior of the last two pseudo-components is also similar for the beech and fir wood (activation energies of 200 and 176 kJ/mol) whereas the different nature of hemicellulose requires significant changes (activation energies of 147 and 110 kJ/mol, respectively).

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1. Introduction

Thermogravimetry has been extensively applied to investigate weight loss characteristics of biomass fuels. Compared with degradation in inert atmosphere, oxidative degradation has been given considerably less attention. In this case, two main stages are observed representing oxidative degradation of the biomass followed by the oxidation of the charred residue, both associated with peaks in the rates of weight loss curves [1]. The presence of oxygen enhances the degradation of the cellulose component at low temperature, with a sharpening of the peak rate, and the overlapping of the decomposition rates of the chemical components [2–6]. Weight loss measurements are useful to evaluate the feedstock reactivities and, when made under negligible influence of heat and mass transfer effects, can be applied to formulate plausible reaction mechanisms and to estimate the related kinetic parameters. Then kinetic mechanisms can be coupled with the description of transport phenomena to simulate the behavior of practical conversion systems [7–11].

Although commercial thermogravimetric systems have a high precision, the sample temperature is not directly measured or controlled. In the presence of oxygen, given the high exothermicity of the combustion reactions, a thermal runway may occur with the temperature inside the sample becoming considerably higher than that foreseen by the assigned program and the sample being oxidized at high reaction rate. These problems have been extensively discussed in previous literature [1,12–15]. As the highest reaction rate in an experiment is roughly proportional to the sample mass and the heating rate in the kinetic regime, in addition to being obviously dependent on the reactivity of the given sample and on the oxygen partial pressure [15], the sample mass should be adequately reduced until no difference is seen in the normalized weight loss curves. In this way it is also guaranteed that spatial temperature gradients are negligible and oxygen diffusion is not the limiting process. Unfortunately, numerous thermogravimetric measurements reported in literature about biomass combustion show the occurrence of thermal runaway, with the consequent formulation of erroneous reaction mechanisms. Moreover, there are still other aspects that should be taken into account when chemical kinetics is the subject of interest.

A significant number of studies is available where, in addition to the determination of the weight loss characteristics, the examination of the data has led to mechanisms of different complexity with kinetic parameters, in particular the activation energies, dependent on the conversion level and/or the heating rate such, for instance, in Refs. [16–18]. In other cases, only a single heating rate is considered (see, for instance, Refs. [19–22]). These models although based on experimental data apparently not impugned by heat and mass transfer effects, are not truly valid over widely variable conditions. Indeed, only kinetic models capable of explaining the shift in the thermogravimetric curves with the heating rate, without changing the kinetic parameters, can be considered potentially correct [23]. Kinetic models with these features for the oxidation of wood and biomass have also been proposed [6,13,23–34], based on the analysis of several thermogravimetric curves obtained under variable heating conditions, with invariant kinetic parameters. The

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Table 1
Chemical composition of wood and residues.

	Extractives [% wt]	Lignin [% wt]	Holocellulose [% wt]	Ash [% wt]
Beech	2.0	22	78	0.2
Douglas fir	2.6	30	67	0.5
Hazelnut shells	9.2	33	56	1.4
Olive husks	8.7	28	61	2.5
Wheat straw	4.9	23	66	6.2

large majority assumes a mechanism of N reactions with n-order kinetics but a distributed activation energy model (DAEM) for the devolatilization stage has also been proposed [29,33,34]. It is, however, extremely difficult to select the best model because, in the first place, the number of reaction steps has been varied from two (a global reaction for biomass devolatilization and a global reaction for char oxidation) up to nine (devolatilization and/or oxidation of the pseudo-components and oxidation of the related char fractions). Moreover, the estimated kinetic parameters vary over very wide intervals. Although the differences in the nature and properties of the biomass fuels (i.e. chemical composition including content and composition of inorganic matter), the experimental conditions (i.e. actual heating conditions), the mathematical treatment of the data (for instance, use of integral or differential data) and magnitude of the deviations between predictions and measurements may explain such a variety of mechanisms and the wide range of variation in the kinetic parameters, the formulation of unified mechanisms valid for a significant number of biomass fuels, with small differences in the kinetic parameters, is highly desirable.

In this study thermogravimetric measurements are made, at several heating rates, for the oxidation of wheat straw, olive husks and hazelnut shells. A peculiar thermogravimetric system is employed which is based on the measurement and control of the sample temperature, thus allowing the reactions to take place under exactly known thermal conditions. Also, the sample mass is accurately determined so as there is no limitation introduced by oxygen diffusion. The weight loss curves, together with two previous sets of data for beech and fir wood, also carefully determined, are applied to understand whether a unified kinetic mechanism can be formulated with activation energies invariant with the lignocellulosic material.

2. Materials and methods

2.1. Materials

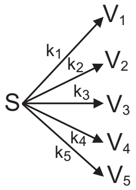
The materials examined in this study are two wood species, beech (Fagus sylvatica) and Douglas fir, which can be considered representative of the usual standards for the hardwood and softwood category, and three agro-industrial residues, hazelnut shells, olive husks (a by-product in the manufacture process of olive oil in mills and consisting of pulp, peel and pits) and wheat straw. The chemical composition is listed in Table 1 [35]. Prior to thermogravimetric tests, samples have been milled to powder (particle sizes below 80 μm) and pre-dried for 10 h at 373 K.

2.2. Experimental details

Solid conversion can be made to occur under known thermal conditions with a proper control of the sample temperature (measured by a close-coupled thin thermocouple), using the intensity of the applied radiative heat flux as the adjustable variable. This principle has been applied in the development of the thermogravimetric system used by this research group [12,13,36,37]. The characteristic size of the process is the thickness of the sample layer, whose limit value for a kinetic control depends on the nature of the solid fuel. For wood and residues, it has been observed that values up to 120 μm allow a good temperature control to be achieved, given maximum heating rates of 40 K/min and a final temperature of 873 K. Also, the weight loss curve is the same as the sample layer thickness is decreased below 120 μm, indicating that conversion is not affected by heat and mass transfer effects. Hence, the tests have been made for sample layers about 110 μm thick (5 mg distributed over a surface 25 mm × 5 mm) using a final temperature of 873 K. The thermogravimetric curves for the two wood species were already available [13] and were obtained with heating rates of 5, 10, 20 and 40 K/min. Those for the residues have been measured for heating rates of 5, 10, 20 and 30 K/min. Each thermogravimetric test has been made in triplicate, showing good repeatability. Maximum deviations between the measured weight loss curves are always in the range 0.1–0.3%.

2.3. Kinetic mechanism

As anticipated, lignocellulosic fuel devolatilization, in both pyrolysis and combustion, has been extensively modeled assuming that volatiles are released according to a set of parallel reactions for lumped components [1,6,18,23,28–34,38]. Then, the overall mass loss rate is a linear combination of the single component rates. The mechanism proposed here for the description of the two main reaction zones (solid devolatilization and char combustion) consists of five independent parallel reactions as follows:



(a1)
(a2)
(a3)
(a4)
(a5)

where S is the solid sample which produces the lumped volatile products V_i (i = 1,5). From the chemical point of view, reactions a1–a3 are associated with solid fuel devolatilization, in relation to the decomposition of the three pseudo-components hemicellulose, cellulose and lignin, and reactions a4–a5 with char combustion, specifically devolatilizion and actual combustion. From the physical point of view solid devolatilization and char combustion are sequential processes but the parallel reaction mechanism is more flexible as it can easily guarantee this feature by an appropriate set of parameter values and, at the same time, can describe well the possible overlap between reactions pertinent to either the devolatilization or the combustion stage. The reactions rates present the usual Arrhenius dependence (A_i are the pre-exponential factors and E_i the activation energies) on the temperature and a linear (reactions a1–a4) or a power law with exponent n (reactions a5) dependence on the solid mass fraction. The latter treatment takes into account the evolution of the pore surface area during conversion [1]. Since the sample temperature, T, is a known function of time, the mathematical model consists of five ordinary differential equations for the mass fractions, Y_i, of the reacting solid fuel:

$$\frac{dY_i}{dt} = -A_i \exp\left(-\frac{E_i}{RT}\right) Y_i^{ni}, \ldots, \ Y_i(0) = \nu_i, \ i = 1, \ldots, 5 \qquad (1\text{–}5)$$

where ν_i, indicated in the following as stoichiometric coefficients, are the initial mass fractions of the lumped classes of volatiles generated. The kinetic parameters are estimated through the numerical solution (implicit Euler method) of the mass conservation equations and the application of a direct method for the minimization of the objective function, which considers simultaneously both integral (TG) and differential (DTG) data for the various heating rates, following the method already described [39].

Some considerations should be made in relation to the use of a five reactions mechanism to describe the combustion of biomass. It has been previously shown [13] that weight loss curves of beech and fir wood combustion can be described by a four-step mechanism. In this approach the devolatilization stage is described by means of two pseudo-components which mainly correspond to hemicellulose and cellulose with the lignin contribution distributed between the two. It seems plausible that the absence of a specific reaction for the contribution of the lignin component is the chief reason for the large variation of the stoichiometric coefficients with the heating rate (0.31–0.41 or 0.23–0.47 for the first reaction, 0.36–0.30 and 0.43–0.32 for the second reaction for fir and beech wood, respectively, given heating rates of 5–40 K/min). Instead, the three-reaction mechanism based on the evolution of the main chemical components, for the devolatilization of wood in inert atmosphere and widely variable heating rates (3–108 K/min) [40] and resulting in kinetic parameters (and component dynamics) significantly different from those determined at a single slow heating rate [41], produces almost constant stoichiometric coefficients. This feature is highly desirable when kinetic mechanisms are incorporated in transport models where average values are generally used. It is understandable that a highly accurate description of solid devolatilization may require a higher number of steps (i.e. extractive decomposition and multiple steps for hemicellulose and lignin decomposition) but it is generally accepted and documented that three is the minimum reaction number which can produce results acceptable for practical applications. Also, it has been shown [37] that the combustion of lignocellulosic chars requires at least two reactions, as the inclusion of a devolatilization stage results in rather high activation energies of the actual combustion reaction, so taking correctly into account the strong influence of the temperature. Thus a minimum number of five reaction steps is required to build up a mechanism that can be applied for different fuels and widely variable heating conditions. Moreover, based on these considerations, the initial guesses for the parameters to be estimated are assumed to coincide with those previously obtained for beech wood in nitrogen [40] for the reactions of the devolatilization stage and for beech wood char [37] for the stage of char oxidation. These two sets of data can be considered representative of the current state of the art in the kinetic modeling of biomass devolatilization and combustion [1,38].

3. Results

The main characteristics of the thermogravimetric curves for the various fuels are discussed first. Then, following the illustration of the evaluation strategy, the results of the kinetic analysis are presented with a comparison between predictions and measurements.

3.1. Thermogravimetric characteristics

The integral and differential curves measured for the two wood species and the residues, showing two main zones (devolatilization and combustion), are compared in Fig. 1 for a heating rate of 5 K/min. The corresponding characteristic parameters are summarized in Table 2. These include the peak rates for the devolatilization and the combustion stages, $-\mathrm{d}Y_{\mathrm{peak1}}/\mathrm{d}t$ and $-\mathrm{d}Y_{\mathrm{peak2}}/\mathrm{d}t$, their positions, in terms of temperatures, T_{peak1} and T_{peak2}, and corresponding mass fractions, Y_{peak1} and Y_{peak2}. Other parameters are the char yield, Y_{c}, and the full width of the rate curve at half maximum, FWHM. The char yield is defined as the solid mass fraction corresponding to the steep decay in the decomposition rate [30] (the corresponding temperature, T_{c}, is also introduced as it can be useful to identify the conclusion of the devolatilization stage) whereas FWHM is defined as in Ref. [42].

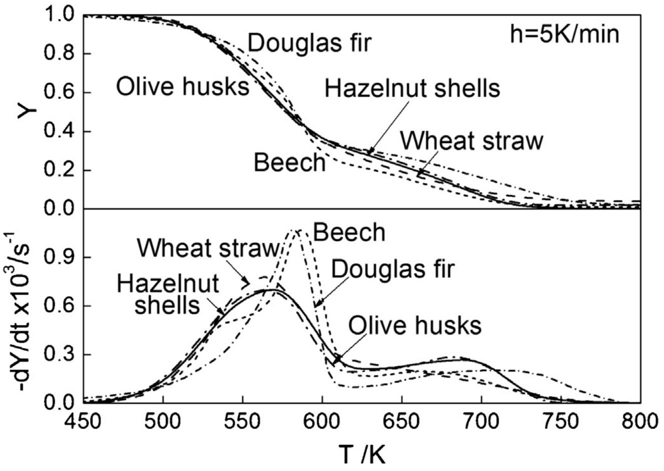


Fig. 1. Measured weight loss curves versus temperature for the various materials at a heating rate of 5 K/min.

On the whole, the devolatilization stage presents features qualitatively similar for the two woods, on one side, and for the residues, on the other. Although the temperatures for the beginning of the degradation process are not significantly different between the various materials, residues present a peak devolatilization rate which is anticipated (by about 15–20 K) and is lower (by about 35–27%) with respect to the wood species which also are rather similar. As a consequence of the peak anticipation, a separation between the shoulder zone, very clearly shown for beech wood, is not evident despite of the similarities of the chemistry of the hemicellulose component (mainly acetylglucuronoxylans for hardwoods [43] and arabinoxylans for herbaceous biomass [44]). In reality the devolatilization process takes place over a wider temperature interval, as testified by the larger FWHM values, due essentially to the devolatilization of the cellulose component at lower temperature which hinders the attainment of fast rates (comparable with those obtained for the woods). It can be hypothesized that the different quantity and composition of ashes is responsible for such a behavior [45], in particular the larger quantities of alkali metals which anticipate at lower temperatures the reaction process and enhance the formation of char [46,47]. The differences for beech and fir wood reproduce trends already observed in nitrogen atmosphere although the presence of oxygen anticipates the reaction process at lower temperatures [6]. The shoulder in the peak rate curve, due to hemicellulose degradation, is much less evident for fir wood and is slightly delayed but the peak rate is attained at slightly lower temperature. This can be attributed to the different nature of this component mainly consisting of galactoglucomannan [44]. The char yield of residues is comparable with that obtained for fir wood, resulting not only from the comparable contents of lignin, which mainly degrades to char, but also from alkali catalysis (the higher ash content of residues in reality reduces the actual volatile fraction). Finally, the temperature for the conclusion of the devolatilization process of the residues is approximately the same as for the two woods (611–620 K versus 609–620 K).

The position of the second peak (combustion) for the residues is intermediate between that of the two woods. More precisely, the peak for beech wood is anticipated with respect to fir wood, a result also observed for the combustion of chars produced from these two wood species [37]. Thus it is likely that the reactivity of char is influenced, at some extent, by the composition and structure of the wood variety. Wheat straw does not show a well defined peak although the extension of the combustion zone is comparable with that of the other two residues. The peak combustion rate is generally higher for the residues, as a consequence of the higher

Table 2
Thermogravimetric characteristics for the various materials at a heating rate of 5 K/min (peak rates for the devolatilization and the combustion stages, $-dY_{peak1}/dt$ and $-dY_{peak2}/dt$, and corresponding temperatures, T_{peak1} and T_{peak2}, and mass fractions, Y_{peak1} and Y_{peak2}, char yield, Y_c, and corresponding temperature, T_c, full width of the rate curve at half maximum, FWHM).

Parameter	Beech	Douglas fir	Hazelnut shells	Olive husks	Wheat straw
T_{peak1} [K]	587	582	569	564	564
Y_{peak1}	0.43	0.51	0.58	0.61	0.61
$-(dY/dt)_{peak1} \times 10^3$ [s^{-1}]	1.07	1.07	0.70	0.70	0.78
T_{peak2} [K]	661	702	687	683	–
Y_{peak2}	0.13	0.16	0.10	0.14	–
$-(dY/dt)_{peak2} \times 10^3$ [s^{-1}]	0.20	0.20	0.27	0.28	–
Y_c	0.22	0.33	0.30	0.33	0.31
T_c [K]	620	609	620	612	611
FWHM	50.1	41.6	81.3	78.5	73.6

char mass fraction produced (with respect to beech) and the shorter duration of the combustion stage (with respect to fir).

3.2. *Kinetic analysis*

An initial attempt in the procedure of parameter estimation has been made by the simultaneous analysis of the integral and differential measurements obtained for the two wood species and the three residues at the various heating rates and requiring that the activation energies of the various reactions were invariant with the material. It has been found that, with this approach, it is not possible to get estimates of the parameters that give acceptable deviations between predictions and measurements for all the fuels examined. This is not surprising given the large differences between the behavior of wood and residues described above.

Thus, as a second approach, the sets of curves measured for the two woods, on one side, and those measured for the three residues, on the other, have been separately evaluated, requiring that the activation energies and the reaction orders for the two reactions of the combustion stage were independent of the material and that the activation energies for the three reactions for the devolatilization stage were the same for each group of materials. This procedure has proved to produce good results for the residues, whereas for the two wood species it has been necessary to remove the constraint on the constancy of the activation energy for the devolatilization of the hemicellulose pseudo-component. The estimated kinetic parameters and deviations between predictions and measurements are summarized in Table 3 and a comparison between predictions and measurements for the integral and the differential data can be made through Figs. 2–6. In all cases the kinetic model predicts well the conversion process with stoichiometric coefficients, listed in Table 4, only weakly affected by the heating rate (average values can be used with a good approximation). Moreover, to facilitate the comparison of the component dynamics, the predicted profiles for the various fuels are shown in Fig. 7 for a heating rate of 5 K/min.

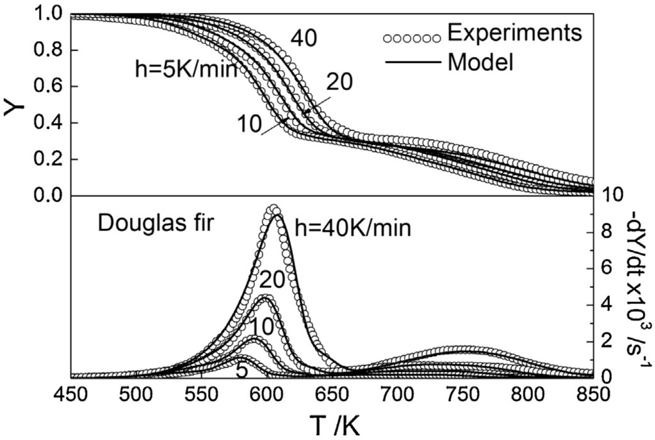


Fig. 3. Comparison between predictions (solid lines) and measurements (symbols) for the integral and differential thermogravimetric curves of fir wood combustion at various heating rates.

The activation energies estimated for the combustion stage are 113 kJ/mol (devolatilization) and 183 kJ/mol (combustion), which are in the range of values generally reported for lignocellulosic fuels [1]. Also, as generally reported, a linear (devolatilization) and a power-law dependence ($n = 1.54$) on the solid mass fraction is found for the two reactions. In general, the combustion stage is quantitatively more important for the samples producing larger

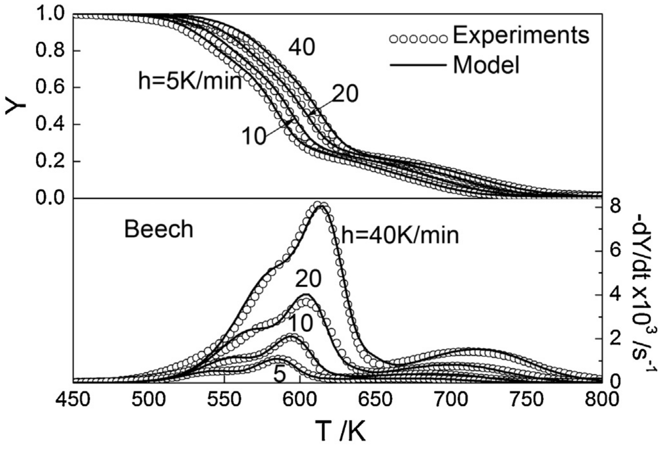


Fig. 2. Comparison between predictions (solid lines) and measurements (symbols) for the integral and differential thermogravimetric curves of beech wood combustion at various heating rates.

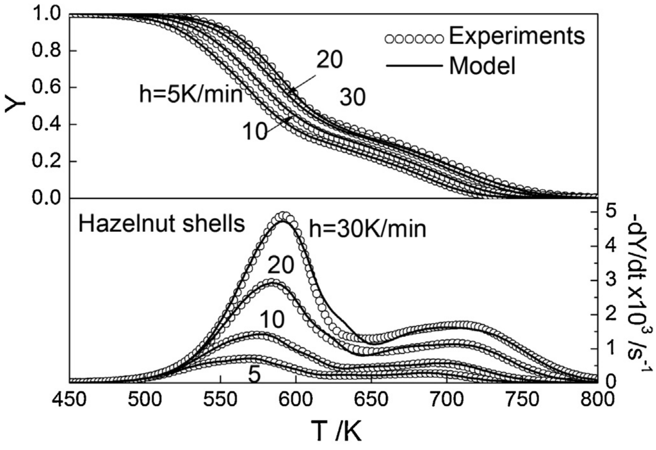


Fig. 4. Comparison between predictions (solid lines) and measurements (symbols) for the integral and differential thermogravimetric curves of hazelnut shell combustion at various heating rates.

Table 3
Estimated kinetic parameters for the five-step reaction mechanism a1–a5 and deviations between predictions and measurements (activation energies, E_i, pre-exponential factors, A_i, reaction order, n).

	Beech	Douglas fir	Hazelnut shells	Olive husks	Wheat straw
E_1 [kJ/mol]	147.0	109.7	125.3	125.3	125.3
A_1 [s^{-1}]	8.74×10^{11}	2.553×10^{8}	7.61×10^{9}	1.02×10^{10}	8.65×10^{9}
E_2 [kJ/mol]	200.4	200.4	170.4	170.4	170.4
A_2 [s^{-1}]	5.02×10^{15}	6.982×10^{15}	2.90×10^{13}	4.06×10^{13}	3.71×10^{13}
E_3 [kJ/mol]	176.0	176.0	163.8	163.8	163.8
A_3 [s^{-1}]	1.17×10^{13}	1.17×10^{13}	1.74×10^{12}	2.19×10^{12}	2.11×10^{12}
E_4 [kJ/mol]	113.0	113.0	113.0	113.0	113.0
A_4 [s^{-1}]	5.60×10^{6}	2.04×10^{6}	8.80×10^{6}	8.59×10^{6}	1.08×10^{7}
E_5 [kJ/mol]	183.0	183.0	183.0	183.0	183.0
A_5 [s^{-1}]	8.81×10^{11}	1.22×10^{11}	6.94×10^{11}	7.07×10^{11}	1.55×10^{12}
n_5	1.54	1.54	1.54	1.54	1.75
% dev_{TG}	0.86	0.93	0.43	0.52	0.36
% dev_{DTG}	2.10	2.28	1.40	1.75	1.71

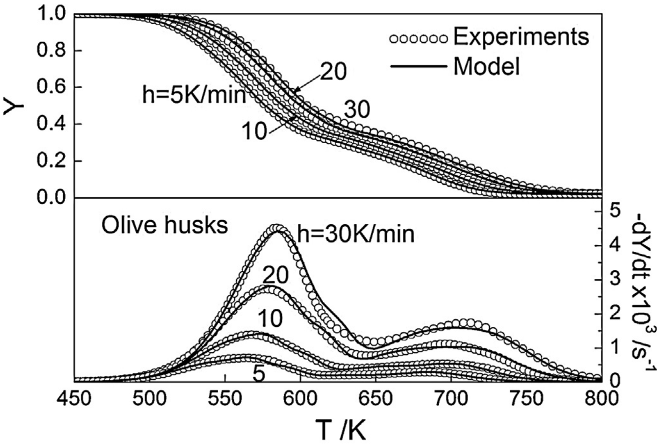


Fig. 5. Comparison between predictions (solid lines) and measurements (symbols) for the integral and differential thermogravimetric curves of olive husk combustion at various heating rates.

quantities of char so depending significantly on the chemical composition of the origin fuel. The total amount of volatiles produced from this stage varies between approximately 25–30% for the two woods and 33–38% for the residues. These figures are higher than the corresponding yields of char listed in Table 1, indicating that the char devolatilization process is somewhat anticipated with respect to the T_c temperatures. Moreover, the analysis of thermogravimetric data of the combustion of char samples [37] indicates that the

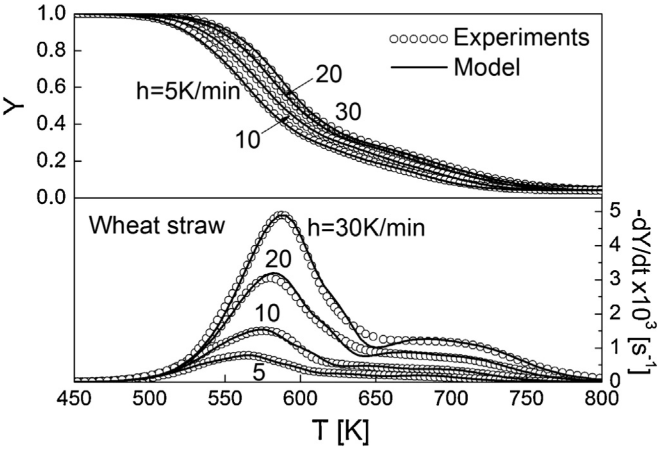


Fig. 6. Comparison between predictions (solid lines) and measurements (symbols) for the integral and differential thermogravimetric curves of wheat straw combustion at various heating rates.

Table 4
Stoichiometric coefficients for reactions a1–a5 on dependence of the heating rate for the various materials. Average values are also indicated.

h [K/min]	Beech				
5	0.22	0.40	0.09	0.13	0.15
10	0.23	0.41	0.09	0.11	0.15
20	0.24	0.41	0.09	0.11	0.14
40	0.24	0.43	0.09	0.11	0.12
Average	0.23	0.41	0.09	0.12	0.14
h [K/min]	Douglas fir				
5	0.15	0.44	0.08	0.14	0.18
10	0.15	0.44	0.08	0.14	0.18
20	0.14	0.46	0.09	0.14	0.15
40	0.14	0.47	0.10	0.14	0.13
Average	0.15	0.45	0.09	0.14	0.16
h [K/min]	Hazelnut shells				
5	0.20	0.21	0.19	0.16	0.24
10	0.19	0.22	0.19	0.16	0.25
20	0.19	0.24	0.17	0.17	0.24
30	0.18	0.28	0.15	0.18	0.21
Average	0.19	0.24	0.17	0.14	0.23
h [K/min]	Olive husks				
5	0.18	0.22	0.20	0.14	0.24
10	0.18	0.22	0.20	0.15	0.23
20	0.17	0.23	0.20	0.16	0.22
30	0.17	0.26	0.17	0.17	0.21
Average	0.18	0.23	0.19	0.16	0.23
h [K/min]	Wheat straw				
5	0.17	0.23	0.20	0.17	0.17
10	0.17	0.23	0.21	0.18	0.17
20	0.17	0.26	0.21	0.16	0.17
30	0.17	0.27	0.21	0.15	0.16
Average	0.17	0.25	0.21	0.17	0.17

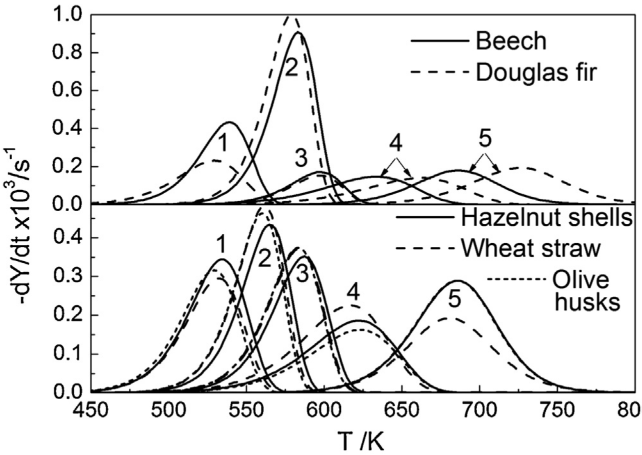


Fig. 7. Predictions of component dynamics for the various materials and a heating rate of 5 K/min.

contribution of the devolatilization step amounts to about 10–25% of the total char mass. Instead, the evaluations made of the data measured for the combustion of wood and residues, despite of the use of the same activation energies, lead to approximately even contributions for the two reactions. This may mean that there is some overlap between the devolatilization processes of the origin fuel and the char and a separation between the two cannot be easily accomplished. Also, it should be observed that the chars examined here have been produced at lower temperatures (T_c values around 610–620 K) while in the other case the chars were obtained at temperatures around 800 K. Hence, it is plausible that the volatile content of the latter is much lower. Component dynamics show that the char devolatilization process takes place over a wide temperature interval (about 520–670 K for the residues, 560–680 K for beech wood and 570–720 K for fir wood). The material differences are obviously taken into account by the stoichiometric coefficients but small variations have also been found for the pre-exponential factors (factors around 5 and 13 for the devolatilization and combustion step, respectively).

The three reactions of the devolatilization stage for the residues present the same activation energies (125, 170 and 164 kJ/mol for the pseudo-components hemicellulose, cellulose and lignin) with variations on the pre-exponential factors by factors of about 1.35, 1.4 and 1.26 in the order. The decomposition of the pseudo-components cellulose and lignin is also very similar for the two wood species, representative of the hardwood and softwood categories, with activation energies of 200 and 176 kJ/mol and small variations on the pre-exponential factor (factors of 1.4 and 1.01). Instead, for the pseudo-component hemicellulose, large variations are required for the activation energy (147 and 110 kJ/mol for beech and fir wood). It can be noticed that, for beech wood, the three activation energies are very close to those previously estimated for inert atmosphere (147, 193 and 181 kJ/mol) [5]. Instead, the lower value estimated for the decomposition of the fir pseudo-hemicellulose is due its low degradation rate (the amount of volatiles released is around 14% versus 23% of beech wood) over the same temperature range (approximately 470–570 K) as for the other wood. Thus, apart from the lower content of hemicellulose in fir wood, it can also be hypothesized that a larger percentage is incorporated in the pseudo-component cellulose. On the other hand, the amounts of volatiles released from pseudo-cellulose are barely higher (45 versus 41%), while the same amount (9%) is produced from pseudo-lignin degradation. It can also be noticed that the temperature range where these two pseudo-components degrade are also the same for the two materials (about 520–600 K and 540–630 K).

The activation energy for the devolatilization of the pseudo-hemicellulose of residues is an intermediate value between those of the two wood species while, for the other two pseudo-components, the values are much lower in accordance with the observed lower rates. Another interesting result is that the amounts of volatiles produced from the three reactions are only weakly affected by the component (17–19%, 24% and 17–21% for the pseudo-components hemicellulose, cellulose and lignin). This indicates that the overlap between the degradation of the three main components is much larger than for woods, as a consequences of the catalytic action exerted by the higher alkali content. The temperature interval where pseudo-components degrade are approximately 470–570 K (hemicellulose), 500–600 K (cellulose) and 520–620 K (lignin) with small variations with respect to those of the two woods reported above.

4. Conclusions

A kinetic analysis has been carried out of thermogravimetric curves for the combustion of wood (beech and fir) and agro-industrial residues (hazelnut shells, olive husks, wheat straw) in the view of formulating a general unified mechanism. It has been found that a five-step mechanism produces good results in all cases and that the two reactions of the combustion stage present the same activation energies (113 and 183 kJ/mol) and reaction order (1 and 1.54) with only small variations on the pre-exponential factors. The three reactions of the devolatilization stage are characterized by the same activation energies (125, 170 and 164 kJ/mol for the pseudo-components hemicellulose, cellulose and lignin) for the three residues again with small variations on the pre-exponential factors. The decomposition of the pseudo-components cellulose and lignin is also very similar for the two wood species, representative of the hardwood and softwood categories, with activation energies of 200 and 176 kJ/mol. Instead, large variations are required for this parameter (147 and 110 kJ/mol for beech and fir wood) for the pseudo-component hemicellulose.

These findings indicate that the devolatilization stage of wood and biomass is significantly different. However unified mechanisms for the biomasses, based on three pseudo-components with the same activation energies, can be developed. The devolatilization of wood requires different activation energies that, for the pseudo-component hemicellulose, also depend on the wood category (softwoods or hardwood). Moreover, the amount of volatiles released from the three reactions is highly different between woods and residues. For these materials there is indeed a much larger overlap between the degradation rates of the various components enhanced by the catalytic action of the larger content of inorganic matter. The differences between wood and biomass are much smaller for the stage of char combustion although these aspects deserved further consideration. In fact this process is located in the tailing zone of the weight loss curves so that the precise details may be in part not clearly shown. Further thermogravimetric measurements carried out with char samples may be useful to shed light on these issues.

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